EPA-99572

PATENT SPECIFICATION (11) 1361027

1361027

(21) Application No. 31365/71 (22) Filed 5 July 1971
(31) Convention Application No. 7 025 201 (32) Filed 7 July 1970 in
(33) France (FR)
(44) Complete Specification published 24 July 1974
(51) International Classification B22C 1/02
(52) Index at acceptance
C3N 25 25A5 25B1 25D1C 25E1 25H1 25H4 25K3E 25K3X

(19)

(54) IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF FOUNDRY MOULDS OR CORES

(71) We, CENTRE TECHNIQUE DES INDUSTRIES DE LA FONDERIE of 12, Avenue Raphael 75 — Paris 16 eme, France; WENDEL-SIDELOR of 6 rue de Wendel — 57 HAYANGE, France and INDUSTRIES CHIMIQUES DE VOREPPE, VOREPPE, (Isere), France, all bodies corporate, organized and existing under the laws of France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The object of the present invention is a method for the manufacture of foundry moulds and cores from a self-hardening liquid sand, making it possible to increase their mechanical resistance.

Previously proposed methods comprise mixing a refractory sand with a binding agent, a hardening agent for the binder, a liquid and a surface-active agent and, without waiting agitating this mixture in order to produce a foam which fluidizes it. The fluidized mixture is thus poured into a vessel containing the pattern of the part to be obtained or having the impression of the core. The mixture sets in a relatively short time thus rapidly allowing handling of the vessel. The resistance continues to increase up to a value such that the mould or core may undergo the metallostatic pressure of the cast metal or metal alloy without appreciable deformation.

The previously proposed liquid sands mentioned above are of the self-hardening type in the sense that it is not necessary to use external agents to make them set, external agents which may be for example, heat or carbon dioxide.

These self-hardening liquid sands may be divided into several categories according to the nature of their constituents.

Certain of these sands comprise, as a binding agent, sodium silicate and, in this case, the setting agent, if it is solid, may be for example:

- silicon or ferro-silicon
- cement
- calcium sulphate or anhydrite
- manganese carbonate
- ferro-chromium slag
- blast furnace slag

or, if it is liquid:

- ethyl acetate or ethyl silicate
- glycollic acid
- polyalcohols

Other self-hardening liquid sands comprise a hydraulic binding agent which may be:

- a cement
- a blast furnace slag

Other self-hardening liquid sands comprise organic binding agents, such as synthetic resins or a mixture of the latter with mineral binding agents.

All these previously proposed methods pursue the following aims:

— allowing filling of the vessel by simple casting, i.e. without packing, due to the fact that the sand is made fluid by foaming.

— obtaining adequate consolidation of the sand in the shortest time in order to recover without delay the aforesaid pattern or core box.

— to produce a mould or a core, whose mechanical resistance over a period is sufficiently compatible with the manufacturing requirements, in order that it can withstand the handling forces and the metallostatic pressure of the cast metal or alloy.

— to create in the mould or core an optimum porosity for the removal of the gases during the casting of the metal or metal alloy.

[*Price 25p*]

BNSDOCID: <GB_____1361027A__I_>

— to arrange that the sand, after casting the part in the mould or around the core, can be easily removed in the sense that it is possible, by conventional means, to detach the sand which adheres to the surface of the part or is trapped in the narrow parts of the latter.

In fact, the previously proposed methods do not make it possible to fulfil all these aims. Moreover, they have certain disadvantages.

A first disadvantage is that the moulds or cores obtained have an inadequate mechanical resistance, both when cold (10daN/cm² at the end of 24 hours with the best known method in this respect) and hot (2.5daN/cm² at 1200°C by this known method).

In fact, when the height of the part and, consequently, the metallostatic pressure are relatively high, the mould is deformed at the base and at this point the part has a bulge. In addition, in the particular case of cast iron, in which graphite causes an expansion on forming, the mould is also deformed. In any case, it is necessary to provide excessively large shrinkage heads in order to avoid pipes.

Moreover, it will be noted that despite numerous and considerable pieces of work, it has never been possible to increase the mechanical resistance of the moulds or cores obtained according to these previously proposed methods, whatever the physical means used; pressure, vibrations, agitations etc., means which are normally effective with non-liquid sands.

A second disadvantage is that the bubbles in the foam only burst a long time after the setting of the sand has begun, in such a way that the condition of the mould surface, in particular in the part which will be in contact with the molten metal, is poor. Thus, in order to improve the condition, it is necessary to apply to this surface a slip which fills up the small superficial holes. But this slip is troublesome and it detracts from the moulding precision, which may be a hindrance in certain cases, since it forms an uncontrolled extra thickness.

A third disadvantage of certain of these previously proposed methods resides in the fact that the mould or core obtained is not permeable or in any case is insufficient for allowing satisfactory escapes of the gases at the time of casting the metal or alloy.

A fourth disadvantage of certain of the said previously proposed methods is that the setting time of the mould or core before its displacement towards the pig-bed is too long if the amount of accelerator is not drastically increased.

The object of the invention is to obviate or mitigate these disadvantages by firstly making it possible to increase, substantially, the hot and cold mechanical resistance of the moulds and cores obtained. Thus, these moulds or cores may withstand very high metallostatic pressures without any deformation. Better still, they effectively oppose any expansion of the cast metal or alloy, such that the precision of the part obtained, even when it is made of graphitic cast iron, is retained and that the compactness of this part is increased, an increase which is translated into a substantial increase of the density. Moreover, when a lesser resistance is adequate, the cost of the primary materials used may be reduced, thus decreasing the quantity of binding agent used. In any case, with the same resistance, the quantity of liquid sand necessary for forming the mould or core may be much less, which allows the cost price of the latter to be reduced.

The aforesaid object is also achieved by producing an automatic stopping up of the superficial micro holes, before the setting of the sand, in such a way that the surface condition of the mould or core is good enough to avoid the use of a slip or in any case to greatly reduce the quantity used of the latter. This object is also attained by systematically producing a permeability of the mould or core at least equal to that of silico-clay sands.

This object is finally attained by greatly decreasing the setting period of the liquid sand, in such a way that the immobilization of the patterns and the cores is reduced to a minimum and the metal or metal alloy may be cast much sooner.

According to the present invention, there is provided a method for producing foundry moulds and cores having a high mechanical resistance comprising mixing a liquid, a refractory sand, an alkali metal silicate as a binding agent, either a blast furnace slag, a ferro-chromium slag or a cement as setting agent which reacts with the binding agent without evolution of gas and a surface active agent to form a self hardening liquid sand and pouring this liquid into a mould, wherein the surface active agent used produces a foam which begins to subside before the sand begins to set and is at least one compound where aqueous solutions fulfil the two following experimental criteria.

(1) they have a section of stretching of the sheet of maximum length, as hereinafter defined, for molar concentrations of the surface active agent of between M/5 and M/50; and

(2) they give a foam whose volume is reduced by at least half in 5 minutes for a molar concentration of M/20.

According to a particularly advantageous embodiment of the method, the density of the sand is increased by applying to the latter pressure and/or repeated mechanical stresses by vibrations and agitation between the time when the sand becomes permeable and the time when it begins to set.

In order that a surface active agent may be used according to the method of the pre-

BNSDOCID: <GB_____1361027A_I_>

sent invention, it is necessary, on the one hand, that its surface active properties are such that it allows the sand mixture to fluidize and, on the other hand, that it produces a foam, the duration (or stability) of which is such that the foam is destroyed in its entirety or at the very least in a large proportion before the sand begins to set.

Numerous surface active agents have been studied on the one hand for their surface active properties, and on the other hand for the stability of the foam of aqueous solutions of these surface active agents, in variable concentrations; and it has been found that any surface active agent fulfilling both experimental criteria, one of which makes it possible to evaluate the surface active properties and the other the stability of the foam of its aqueous solutions at a given molar concentration, can be used in the method according to the invention.

In order to evaluate the surface active properties of the surface active agents, there was used the technique described by J. Vallee et al. (Revue Francaise desCorps Gras, October 1956, Page 676 and November 1956 Pages 1—9) and based on the stretching of their aqueous solutions into a thin sheet. The measurements are taken with the recording tensiometer of Prof. J. Thibaud [C.R. Acad. Sci. Vol. 211, Page 355, (1940) and Journal de Physiquie 1940, page 26]. This device is essentially constituted by a three sided device of platinum wire, connected to the arm of a balance, the other end of which has a mirror which reflects an incident light beam towards a recording plate. The device is submerged in the solution to be studied contained in a vessel which is displaced at constant speed up and down. When the vessel descends and the horizontal blade of the device is about to leave the solution, it is retarded by the film or the thin sheet which is formed between the blade and the free surface of the solution studied. The result is a variation of the position of the arm depending on the surface tension, and a displacement of the light spot which, being subject simultaneously to a movement of horizontal translation, describes a curve as a function of time on the recording plate.

After an ascending part corresponding to the appearance of the surface tension, this curve has a flat section corresponding to the stretching of the thin sheet between the horizontal blade of the device and the free surface of the liquid studied. The flat section is interrupted at the moment when the sheet breaks, and since the stretching speed is constant, the length of the flat section recorded is proportional to the stretching length of the thin sheet before its rupture.

According to the studies made by J. Vallée and reported in the above mentioned articles, the length of the flat section of the stretching of the sheet on the curves thus traced varies as a function of the molar concentration of the surface active agent of the aqueous solution and passes through a maximum which corresponds to the beginning of the aggregation of micelles in the solution.

In this way, for numerous surface active agents, which may be used for fluidizing the sand mixtures, the molar concentration of their aqueous solutions has been determined for which the flat section of stretching of the sheet has a maximum length.

There has also been measured, for the same surface active agents, the foaming power of aqueous solutions in various molar concentrations of the surface active agent, according to the standard NF-T-73404; and there has been noted the volume of foam formed at the end of 30 seconds, 3 minutes and 5 minutes, respectively, after dropping from a height of 450 mm, 500 ml of solution onto a liquid surface of the same solution. All the measurements were taken at a temperature of between 20—25°C.

It has been found that, in the case of self-hardening liquid sands, the binding agent of which is an alkali metal silicate, the density of the sand is increased and, consequently, the mechanical resistance of the moulds, according to the method of the invention, by using as a surface active agent, at least one compound, whose aqueous solutions fulfil the two following criteria:

They have a maximum flat section for the stretching of the sheet for molar concentrations comprised between M/5 and M/50, preferably M/20;

They give a foam whose volume is reduced by at least half in five minutes, for a molar concentration of M/20.

The following table gives, for a certain number of compounds having surface active properties, on the one hand, the length of the flat section of stretching of the sheet for solutions of molar concentration M/5, M/10, M/20, M/50, M/100, on the other hand, the volumes of foam measured 30 seconds, 3 minutes, and 5 minutes after the end of the fall of solutions of molar concentrations M/20, M/50 and M/100.

The length of the flat section of the stretching of the sheet is expressed in millimetres on curves recorded for a stretching speed of 1 centimetre per minute, with a device of platinum wire of 1/10th of a millimetre diameter, whose horizontal blade has a length of 3 centimetres, a recording of 1 centimetre of length on the curve corresponding to a stretching of 1 millimetre for the thin sheets formed.

The volume of foam is expressed in millilitres.

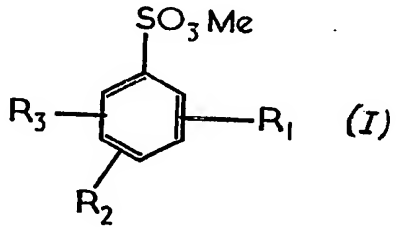
According to this table it can be stated that, the two criteria abovementioned are fulfilled on the one hand, by alkylbenzene sul-

BNSDOCID: <GB_____1361027A_I_>

phonates, such as mono- and di-ethylbenzene sulphonates, mono- and di-isopropylbenzene sulphonates, n-propylbenzene sulphonate, and n-hexylbenzene sulphonate, and on the other hand by an alkali metal alkylsulphate which is the octylsulphate.

Each of these compounds fulfilling the two above mentioned criteria are used in the densification method according to the invention, applicable to sands, the binding agent of which is an alkali metal silicate, in the proportion of 0.005 to 2% by weight of the surface active compound relative to the total weight of the liquid sand.

In addition, it has been found that one can use, as a surface active agent in the densification method according to the invention applicable to sands, whose binding agent is an alkali metal silicate, a mixture of two or more alkyl benzene sulphonates of the following formula:



(I)

(in which Me represents an alkali metal or HX, X being an amine, R_1, R_2, R_3 each representing an atom of hydrogen or a straight or branched chain alkyl group containing 1 to 6 carbon atoms) or a compound of the formula I used alone and wherein R_1 represents a hydrogen atom, R_2 is a hydrogen atom or a C_2, C_3 or C_6 alkyl group and R_3 is a C_2, C_3 or C_6 alkyl group; the surface active agent being used in the proportion of 0.005 to 2% by weight relative to the total weight of liquid sand.

One can see from the table, that certain alkali metal alkylbenzene sulphonates of formula I do not fulfil simultaneously the two abovementioned criteria; alkali metal, such as sodium, p-toluene sulphonate does not foam at the tested concentrations; alkali metal triisopropylbenzene sulphonate has a maximum flat section of stretching of the sheet for a concentration slightly above M/50; alkali metal n-butylbenzene sulphonate gives foams which are too stable, and the volume of which does not decrease by half after five minutes. In fact, it was found that each of these compounds may not be used alone as a surface active agent in the method according to the invention, but only in a mixture of these compounds or with other alkyl benzene sulphonates of formula I as above such as alkali metal ethyl and di-ethylbenzene sulphonates, n-propyl benzene sulphonates, isopropyl and di-isopropyl benzene sulphonates and hexyl benzene sulphonates or with an alkali metal octylsulphate.

It was also found that, on the one hand the alkali metal alkylbenzene sulphonates whose alkyl chain contains more than 6 carbon atoms, such as octylbenzene sulphonate and dodecylbenzene sulphonate and on the other hand lauryl sulphate, compounds whose aqueous solutions according to the following table do not fulfill the two criteria mentioned in the above are surface active agents which, when they are used alone as surface active agents do not make it possible to make the sands, whose binding agent is an alkali metal silicate, more dense according to the method of the invention.

Embodiments of the method are described hereafter as non-limiting examples, these same examples being accompanied by curves intended to show the chronology of the phenomena which occur after the pouring of the sand.

The applicants have ascertained, after numerous experiments, that the mechanical resistance of the mould could be increased to a large extent if the mixture of liquid sand was made more dense before it solidified. To be more exact, tests have shown that, in order to obtain this densification, it is necessary that the foam produced by the surface active agent is destroyed in its entirety or at the very least in a large proportion before the mixture begins to set.

In order to illustrate in an indisputable manner, the chronological order of the phenomena, curves have been drawn for each of the examples taken and explained hereafter.

These curves are as follows: —

1 — A curve of the compression of the sand as a function of time, showing from what moment the sand sinks in the vessel and the significance of this settling;

2 — A curve of the setting of the sand as a function of time, showing at which moment the solidification of the sand begins;

3 — A permeability curve as a function of time showing from which moment the bubbles of the foam which burst join together, thus conferring a certain permeability on the sand.

The curves in question have been drawn for all the experiments carried out and, in particular, for those of the examples described hereinafter, proceeding as indicated below;

1 — All the self-hardening liquid sands subject to the experiment are measured out with a view to conferring on them the same fluidity at the moment of casting. For measureing this fluidity an Abrahms cone is used whose small base has a diameter of 100mm, whose large base has a diameter of 200mm and which has a height of 300mm. This cone, whose larger open base is placed

BNSDOCID: <GB_____1361027A__I_>

on the plate, is filled with liquid sand at its small base by pouring directly into it a stream of liquid sand. The cone is then separated from the plate and the sand spreads over the latter. For the examples given hereafter, the fluidity of the sands tested is such that the diameter over which the latter spreads on the plate is comprised between 360 and 370mm;

2 — In order to measure the compression, a cylindrical vessel is used, whose diameter is 160mm and whose height is 540 mm, this vessel is filled by pouring the liquid sand leaving the mixer and the settlement or drop in level of the sand is measured as a function of time. Thus the graphs illustrating the examples 1—7 are obtained, the curves drawn in fine unbroken line being designated by the general reference 1. In these graphs, the y axis represents the compression T expressed in millimetres on a linear scale, and the x axis the time t expressed in minutes on a logarithmic scale, the origin of time corresponding to the moment of the pouring of the sand at the output of the mixer into the aforesaid vessel;

3 — The setting of the said has been shown by measuring the threshold of shearing or consistency.

In order to measure the threshold of shearing, the aforesaid vessel (diameter of 160mm and height of 540mm) is filled with liquid sand poured directly from the mixer, the sand is allowed to settle naturally until lowering of the level is no longer appreciable, and there is cut from the base of the cylinder of sand thus obtained a cake 40mm in height. The density of the sand in this cake is, according to the mixtures between 1.34 and 1.38. In order to determine the shearing threshold, a Vicat needle having a section of 1 millimetre squared according to the standard P15414 of 1960 is used, the depth of penetration of this needle loaded with variable masses is measured and, according to the Metro's formula, one calculates, depending on this depth and the corresponding total mass, the shearing threshold expressed in dynes/cm^2.

There were thus obtained, on the aforementioned graph, curves in fine broken line designated by the general reference 2. In these graphs the y axis represents on a logarithmic scale the shearing threshold SC expressed in dynes/cm^2 and the x axis represents the time T as previously.

The setting begins when the rheological properties of the mixture change. Now, the curves 2 of all the examples (Figs. 1—14) show that the shearing threshold first of all remains substantially constant then subsequently increases very rapidly but the transition is progressive. The rounded part 5 of the curve which translates this transition does not make it possible to define the beginning of the setting accurately. We will thus consider, in the following, that the beginning of setting is defined by the point A of intersection of the tangents to the rounded part 5 extending the substantially linear part 6 and 7 of the curves 2.

Another test is carried out causing an additional settling of the sand by vibrations or agitation. The vibrations last for 10 seconds for each test. The amplitude of agitation is 40mm and there are 10 or 20 in number. In all the cases, an overall settling is thus produced, which according to the mixtures varies between 60 and 160mm which corresponds to a cake density of between 1.5 and 1.7.

This test makes it possible to obtain on the same graphs the curves in thick broken line designated by the general reference 3.

4 — In order to measure the permeability a cylindrical tube of 50.8mm diameter is used, the base of which is perforated and the liquid sand leaving the mixture is poured into this tube. The depth of this tube is such that the height of the sample of sand after natural settling is equal to 50.8mm. The tube containing the sample is mounted on an automatic Dietert No. 335-A permeameter. This apparatus indicates an index of permeability or a AFS index which depends on the time required for a determined volume of air under a given pressure to pass through the sample of sand.

The measurements are translated by the curves drawn on the same graph as previously in thick unbroken line, and are designated by the general reference 4. For these curves 4, the x axis represents the time t with the same scale as the other curve and, the y axis represents the permeability expressed in AFS index and drawn on a linear scale.

All measurements were made at a temperature of 18—20°C. The following examples are intended to illustrate the invention without in any way limiting its scope.

EXAMPLE 1. (Fig. 1).

A liquid sand is made with the following constituents:

- 50kg of silica sand, the mesh size of which is 55—60 AFS(American Standard);
- 3.5kg of ground, granulated blast furnace slag, the surface area of which is 3300 ± 200cm^2/g and the basicity index of which is 1.35;
- 2.5kg of sodium silicate, the SiO_2/Na_2O modulus is equal to 2, and the content of dry material is 51%
- 1.6kg water
- 50g of commercial sodium mono-isopropylbenzene sulphonate (40% pure product) constituting the surface active agent.

For the tests, a Henry Mixer of the type N1001 is used the rotor of which with radial

BNSDOCID: <GB_____1361027A__I_>

paddles is driven by a horizontal shaft mounted to rotate in a cylindrical vessel of 360mm diameter. This rotor is moved at a speed of 104rpm. The aforesaid dry components are introduced into the vessel and are mixed for 1 minute, then the liquid products are introduced and the mixing continues for 2 minutes.

At the end of this time, the liquid sand obtained is poured into the vessel for measuring settlement, into the vessel for obtaining the cake serving for the measurement of the shearing threshold and into the tube for measuring permeability. Then, the curves 1 to 4 are traced as described in the aforesaid. These curves are illustrated by the graph of Fig. 1.

The curve 1 shows that the foam begins to subside 30 seconds after pouring and subsides naturally for 1 minute 30 seconds in order to achieve a settling of 25mm for an original height of 540mm.

The curve 2 shows that the consistency of the mixture does not develop for more than 10 minutes, but that subsequently it increases very rapidly, the beginning of the setting of the sand, defined as above indicated, taking place 20 minutes after the pouring.

By comparing these two curves, it can be ascertained that the mixture subsides considerably and is, consequently, more dense before the setting begins.

The curve 4 shows that the permeability of the mixture is zero for 2 minutes 30 seconds and that it increases subsequently very rapidly.

The sand can be subjected to repeated mechanical stresses, by vibrating it by means of an external vibrator, a needle, a vibrating table or the like, or by agitating it by means of an agitating table for example. If these stresses last for 2 minutes 30 seconds after pouring, i.e. when the permeability begins to develop but when the setting has not yet begun the experiment confirms that the setting of the mixture is much greater than normal; it happens from 25 minutes to 125 minutes. Under these circumstances, the sand becomes more dense than formerly since its apparent density is 1.57 instead of 1.38 obtained by natural settling. Naturally, it can be noted referring to curve 3, that this densification, if it has the immediate effect of slightly increasing the consistency, nevertheless does not have the effect of starting the setting since the consistency remains constant for a certain time after the vibration and only begins to increase at the end of 20 minutes, i.e. a certain time after the beginning of the permeability.

EXAMPLE 2. (Fig. 2)

A liquid sand is made with the same constituents as in Example 1, but with 2.5kg of blast furnace slag instead of 3.5kg and using as a surface active agent 8g of commercial sodium di-isopropylbenzene sulphonate which is 40% pure product.

The curves 1 to 4 obtained are illustrated in Fig. 2. These curves confirm the results of Example 1, namely:

— that the sand settles and becomes more dense before setting (comparison of curves 1 and 3);

— that the beginning of setting occurs after the moment when the permeability appears (comparison of curves 3 and 4) which makes it possible to increase the densification by vibrating the sand as soon as it becomes permeable.

On the other hand the subsidence of the foam occurs later than in Example 1, which allows more time for pouring the sand whilst it is still fluid.

EXAMPLE 3. (Fig. 3)

A liquid sand is produced with the same constituents as in Example 1, but using as a surface active agent a mixture of 25g. sodium mono-isopropylbenzene sulphonate and 5g. sodium di-isopropylbenzene sulphonate each of these products being 40% pure.

The curves 1 to 4 obtained are illustrated in Fig. 3 these curves confirm the results obtained previously and show that by using the mixture of surface active agents, particularly favourable conditions are produced for obtaining moulds of liquid sand according to the invention.

In fact the subsidence of the foam is produced only at the end of about 4 minutes, which allows the sand time to be poured. On the other hand, the setting of the sand begins only twenty minutes after the moment when the sand becomes permeable which makes it possible to vibrate it in order to increase its density before it sets.

EXAMPLE 4. (Fig. 4).

A liquid sand is produced in the same way as in Example 1, and by using the same constituents as in Example 1, with the exception of the surface active agent which is constituted in this case by:

9g. of sodium di-isopropylbenzene sulphonate of 40% purity and
12g. of potassium p-toluene sulphonate of 90% purity.

The curves 1 to 4 obtained are illustrated in Fig. 4. These curves confirm the result of the preceding examples namely:

— that the sand settles and becomes more dense before setting (compare curves 1 and 2);

— that the sand becomes more dense when it is vibrated as soon as it becomes permeable (curves 4 and 3). The density of the sand after vibration or agitation reaches 1.67.

Moreover, the comparison of the curves

BNSDOCID: <GB_____1361027A__I_>

1 of Figures 2 and 4 shows that the incorporation of potassium p-toluene sulphonate accentuates the settling of the sand.

EXAMPLE 5. (Fig. 5)

A liquid sand is made by using the same constituents in Example 1 but by using as surface active agent a mixture of 14g. sodium tri-isopropylbenzene sulphonate of 40% purity and 20g. potassium p-toluene sulphonate of 90% purity.

The curves 1 to 4 obtained are illustrated in Fig. 5. They show that the settling of the sand is produced later than in the preceding example, but however, still before the beginning of the setting of the sand. The density of the sand after vibration reaches 1.67.

EXAMPLE 6. (Fig. 6)

A liquid sand is made using the same constituents as in Example 1, but using as a surface active agent 25g sodium di-ethylbenzene sulphonate of 40% purity.

The curves 1 to 4 obtained are illustrated in Fig. 6. They show on the one hand, that the natural settling of the sand reaches 40mm and settling after vibration reaches 149mm, the density of the sand thus being 1.66; on the other hand the setting of the sand only begins at the end of 15 minutes, i.e. more than 10 minutes after the subsidence of the foam.

EXAMPLE 7. (Fig. 7)

A liquid sand is made with the same constituents as in Example 1, but using as a surface active agent 50g. of sodium n-propylbenzene sulphonate, of 40% purity in the place of di-ethylbenzene sulphonate.

The curves 1 to 4 obtained and illustrated in Fig. 7 confirms the results of the preceding example; The sand settles and its density may be increased up to 1.65 by vibrations before the setting begins.

EXAMPLE 8. (Fig. 8)

A liquid sand is made with the same constituents as in Example 1, but using as a surface active agent 100g. of sodium n-hexylbenzene sulphonate which is 40% pure.

The sand still settles clearly before it begins to set and its density may be increased by vibrations up to 1.67 or by agitation up to 1.68.

EXAMPLE 9. (Fig. 9)

A liquid sand is made with the same constituents as in Example 1, but using as a surface active agent a mixture of 5g. of sodium n-butylbenzene sulphonate (40% purity) and 15g. of potassium p-toluene sulphonate (90% purity).

The curves 1 to 4 are illustrated in Fig. 9 and show that the settling begins to increase rapidly only at the end of 5 minutes, but still before the sand sets (15 minutes), which makes it possible to vibrate the sand in order to increase its density up to 1.63.

EXAMPLE 10. (Fig. 10)

A liquid sand is made with the same constituents as in Example 1, but using as a surface active agent 8g of sodium octylsulphate (at 40%). The curves 1 to 4 obtained are illustrated in Fig. 10 and show that the natural settling of the sand is not very considerable; the density may be increased by vibrations or agitations up to 1.68.

EXAMPLE 11. (Fig. 11)

A liquid sand is made with the same constituents as in Example 1, but using as a surface active agent a mixture of 7.5g. sodium octylsulphate (at 40%) and 5g. of sodium benzene sulphonate (at 40%). The curves 1 to 4 obtained and illustrated in Fig. 11 invite the same comments as those of Fig. 5; a sand density of 1.64 may be obtained by vibrations before the sand sets.

EXAMPLE 12.

A liquid sand is made in the same manner as described in Example 1, but with the following components:

- 50kg sand with a mesh size of 100AFS;
- 3.5kg of blast furnace slag;
- 3kg of sodium silicate with an SiO_2—Na_2O modulus equal to 2 and a dry material content of 51%;
- 1.8kg water;
- 50g of sodium mono-isopropylbenzene sulphonate (40% pure); and
- 7g. of sodium di-isopropylbenzene sulphonate (40% pure); and
- 40g. of potassium p-toluene sulphonate (90% pure) constituting the surface active agent.

There is thus obtained, after the sand sets, a mould having the same properties of high mechanical resistance as those obtained in the preceding examples. This example shows that the method according to the invention can be applied to sands having a very high index of fineness, which is particularly advantageous for the manufacture of moulds when non-ferrous alloys will be cast, and which will make it possible to obtain parts having "a fine skin".

EXAMPLE 13. (Fig. 12)

A liquid sand is made with the following constituents:

- 50kg of silica sand the mesh size of which is comprised between 50 and 60 AFS;
- 2.5kg slag coming from the manufacture of ferro-chromium alloys;
- 3kg of sodium silicate the SiO_2—Na_2O modulus of which is 2.8 and the dry material content is 48%
- 1.kg water;
- 20g. of sodium di-isopropylbenzene sulphonate at 40% purity and

BNSDOCID: <GB_____1361027A__I_>

— 20g. of sodium mono-isopropylbenzene sulphonate at 40% purity.

The curves 1 to 4 obtained are illustrated in Fig. 12. The density of the sand after vibration reaches 1.69.

These curves confirm the results obtained with Examples 1 to 12 which show that the method applies not only to sand containing blast furnace slags as a setting agent, but also to sands whose setting agent is of ferro-chromium slag.

EXAMPLE 14. (Fig. 13)

A liquid sand is made as in Example 1, with the following constituents:

— 50kg sand;
— 3.2kg sodium silicate;
— 1.25kg water;
— 2kg of an artificial Portland cement CPA325;
— 25g. of sodium di-ethylbenzene sulphonate at 40% purity.

The curves 1 to 4 obtained are illustrated in Fig. 13. A very considerable natural settling is obtained; 55mm. And, although the beginning of setting took place much sooner than in the preceding Examples (4 minutes), the sand may reach a density of 1.68.

This Example shows that the method applies not only to sand whose setting agent is a blast furnace slag or ferro-chromium slag, but also to sand whose setting agent is cement.

EXAMPLE 15. (Fig. 14)

A liquid sand is made with the same constituents as in Example 1, but by replacing 70% of the new sand by regenerated sand of the same mesh size and by using as a surface active agent a mixture of 25g. of sodium di-isopropylbenzene sulphonate (at 40%) of 5g. sodium diethylbenzene sulphonate (at 40%) and of 10g. potassium p-toluene sulphonate (at 90%).

The curves 1 to 4 obtained are illustrated in Fig. 14.

The sand settles naturally by 40mm, and since the foam subsides before the sand sets, the density of the latter may be further increased up to 1.59 by vibrations or agitations.

This example shows that the densification method of the present invention is applicable in a case where at least a part of the sand entering the composition of the mixture is constituted by regenerated sand, i.e. sand having already served in the manufacture of moulds and cores, and from which there has appropriately been removed by known means, the products which coat each grain of sand after the casting of metal.

The method of the invention makes it possible to increase the mechanical resistance of moulds and cores obtained with the liquid sand. This property is illustrated by means of the test described below and carried out with the liquid sand of Example 5.

In a first series of cold tests, one attempts to determine the variation of resistance to compression of samples of liquid sand of density equal to 1.38 depending on the storage time, in a confined area and at ambient temperature (22°C).

Several identical samples are obtained by pouring into as many tubes as are required for measuring (8 for example) the liquid sands leaving the mixer. Each tube of 50.8mm diameter and 50.8mm height is provided with an extension tube and the sand which is poured in is loaded in such a way as to be subject for 15 minutes to a pressure of 65 millibars corresponding to that produced in the previous test by the 500mm column of sand which was above the cake. At the end of this time, the extension tube is removed and the tube is level and then one hour after pouring, the test samples are extracted from the tube and kept air free. The density of these test samples is 1.38 as previously.

Every three hours, a sample is subject to a standard test for resistance to compression on a Dynamometric press for example. The breaking load read is expressed in daN/cm².

The curve 8 of Fig. 15 illustrates the variation of this resistance R along the y axis as a function of time t along the x axis and expressed in hours.

A second series of cold tests is effected in the same manner on samples of liquid sands whose density is 1.57. Each sample having the same volume as the others is obtained by pouring into a tube of 50.8mm diameter a mass of sand corresponding to this volume and to this density then by pressing in order to obtain a height of 50.8mm.

A third series of cold tests is effected on samples of liquid sand whose density is 1.67 obtained by the same method as previously but starting with a greater mass of sand and pressing as much as possible.

The curves 9 and 9*a* Fig. 15 are obtained by the resistance test carried out on these samples of density 1.57 and on those of density 1.67.

In a fourth series of cold tests, one attempts to determine at ambient temperature (22°C) the variation of resistance to compression as a function of the density of the sand and at the end of a constant period after the pouring of the sand.

There are thus used samples made with the same sand and in the same way as in the second series of tests, but by varying the quantity of sand pressed into the tubes in such a way that the apparent densities of the said samples are all different from each other.

Curve 10 of Fig. 16 illustrates the variation of the mechanical resistance of the samples,

BNSDOCID: <GB_____1361027A__I_>

reached 1 hour after pouring, as a function of the density d of the samples. Curve 11 of Fig. 16 illustrates the same variation 24 hours after casting.

The analysis of these curves 8—11 shows that:

— The greater the density of the sand, the higher the mechanical resistance achieved;

— The greater the density of sand, the quicker a given resistance is obtained.

Consequently, the moulds or cores can be removed sooner from the bed for pouring the sand. The metal or metal alloy can be cast sooner, i.e. as soon as an adequate resistance of the sand is attained and, consequently, without waiting for it to reach its maximum. There can be obtained moulds which are much more resistant (25daN/cm² for a density of 1.57 and 33daN/cm² for a density of 1.67 at the end of 24 hours, instead of 12daN/cm² for baked silico-clay sands) and consequently able to support much higher ferro-static pressures and more intense expansions. When a lower resistance is adequate it is possible to economise on the cost of primary materials by reducing the proportion of binding agent used. It is possible with an equal resistance of the mould to reduce the thickness of the walls and thus decrease the quantity of liquid sand necessary (400kg per ton of metal instead of 600 with no liquid sand).

All these results are particularly advantageous since they make it possible in the last analysis to reduce the cost price of casting of metal.

In a fifth series of hot tests, one attempts to determine the variation of resistance to compression when hot (1200°C) as a function of the density.

The samples used for these tests are obtained by directly pouring liquid sand at the outlet of the mixer into tubes of 28.6mm diameter and 50.8mm height, these tubes being provided with extensions. The sand is subject to a pressure of 65g/cm². Independently, the tubes are vibrated for a longer or shorter period and at an appropriate amplitude, so as to obtain samples of different densities. Fifteen minutes after the pouring of the sand, the extensions are removed and the tubes are levelled. One hour after pouring, the samples are extracted from the tubes and stored in a limited supply of air for 24 hours.

Each sample is then introduced into an oven heated to a temperature of 1200°C and, at the end of 30 seconds, it is subjected to an increasing compressive load until rupture. For this purpose, one may use the Thermolab Dilatometer apparatus No. 753 made by Dietert. In any case, the rupture load with compression of the sample at a temperature of 1200°C is noted and expressed as previously in daN/cm² in order to show a resistance to compression R when hot.

The curve 12 of Fig. 17 illustrates the variation of this resistance R when hot, on the y axis as a function of the density of the samples on the x axis. This curve shows that the resistance when hot increases with the density of the samples.

Now, it is known that the higher the resistance of the sand when hot, the more precise the geometry of the part obtained and the better the density of its structure. Thus, such sands are particularly appropriate for the casting of parts of graphitic cast iron or of high parts of any alloy.

Moreover, tests show, on the one hand that the inner surface of the mould free from slip is very smooth and, consequently, that the appearance of the skin of the part is excellent, on the other hand, that the sand is very easily removed after casting.

BNSDOCID: <GB_____1361027A__I_>

BNSDOCID: <GB_____1361027A_I_>

TABLE

Measurements taken of the aqueous solutions of various surface active agents.

Surface active agents	M.W.	Surface properties determined with a THIBAULT tensiometer: Length of the stage of stretching of the sheet (in mm.) Molar concentrations of solutions					Foaming power determined according to N.F. T.73.404: volume of foam in ml. after 30 sec., 3 min. and 5 min. Molar concentrations of solutions.								
		M/5	M/10	M/20	M/50	M/100	M/20 30s.	M/20 3m.	M/20 5m.	M/50 30s	M/50 3m.	M/50 5m.	M/100 30s.	M/100 3m.	M/100 5m.
Sodium p-toluene sulphonate	194	0	3	1	0		does not foam								
Sodium ethylbenzene sulphonate	208	0	3	3	0		10	0	0	no longer foams					
Sodium di-ethylbenzene sulphonate	236	0	1	5	0		foam falls before 30 sec.								
Sodium n-propylbenzene sulphonate	222	0	0	3	0	0	foam falls before 30 sec.								
Sodium isopropylbenzene sulphonate	222	2	3	7	2		foam falls before 30 sec.								
Sodium di-isopropylbenzene sulphonate	264	0	0	9	2	3	110	100	50	foam falls before 30 sec.					
Sodium tri-isopropylbenzene sulphonate	306	0	3	11	13		300	80	20	180	60	20	30	20	5
Sodium n-butylbenzene sulphonate	236	0	20	30	7	5	260	220	170	180	160	160	100	50	20
Sodium n-hexylbenzene sulphonate	264	22	35	10	8	8	30	10	0	foam falls before 30 sec.					
Sodium n-octylbenzene sulphonate	294	15	17	20	22		300	50	10	100	0	0	10	0	0
Sodium n-dodecylbenzene sulphonate	348	14	16	12	13		400	380	370	450	430	410	410	380	350
Sodium octyl sulphate	232	36	18	0	2	0	100	50	50	20	10	10	foam falls before 30 sec.		
Sodium lauryl sulphate	288	38	60	55	27		455	430	420	440	420	410	410	390	390

WHAT WE CLAIM IS:—

1. A method for producing foundry moulds and cores having a high mechanical resistance comprising mixing a liquid, a refractory sand, an alkali metal silicate as a binding agent, either a blast furnace slag, a ferro-chromium slag or a cement as setting agent which reacts with the binding agent without evolution of gas and a surface active agent to form a self hardening liquid sand and pouring this liquid into a mould, wherein the surface active agent used produces a foam which begins to subside before the sand begins to set and is at least one compound whose aqueous solutions fulfil the two following experimental criteria:—

(1) they have a section of stretching of the sheet of maximum length, as hereinbefore defined, for molar concentrations of the surface active agent of between M/5 and M/50; and

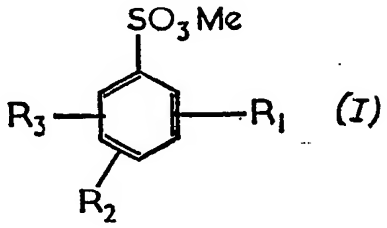
(2) they give a foam whose volume is reduced by at least half in 5 minutes for a molar concentration of M/20.

2. A method according to Claim 1, wherein, in order to increase the density of the sand, pressure is applied to the sand between the time when the sand becomes permeable and the time when the setting begins.

3. A method according to Claim 1, wherein in order to increase the density of the sand, the sand is subjected to repeated mechanical stresses by vibrations and agitation between the time when the sand becomes permeable and the time when it begins to set.

4. A method according to Claim 1, wherein in order to increase the density of the sand, a pressure is applied to the sand and the sand is subjected to repeated mechanical stresses by vibrations and agitation, between the time when the sand becomes permeable and the time when setting begins.

5. A method according to any one of claims 1 to 4 wherein the surface active agent is a mixture of two or more alkylbenzene sulphonates of the formula:



(I)

wherein Me represents an alkali metal or HX, X being an amine, and R_1, R_2, R_3 each represents an atom of hydrogen or a linear or branched alkyl group of 1—6 carbon atoms, used in the proportion of 0.005 to 2% by weight relative to the total weight of the liquid sands.

6. A method according to any one of claims 1 to 4, wherein there is used, as a surface active agent, an alkylbenzene sulphonate of formula (I) according to claim 6 used alone, wherein R_1 represents a hydrogen atom, R_2 represents a hydrogen atom or a C_2, C_3 or C_6 alkyl group and R_3 represents a C_2, C_3 or C_9, alkyl group used in the proportion of 0.005 to 2% by weight relative to the total weight of the liquid sand.

7. A method according to claim 6, wherein the surface active agent is an alkali metal mono-isopropylbenzene sulphonate.

8. A method according to claim 6, wherein the surface active agent is an alkali metal di-isopropylbenzene sulphonate.

9. A method according to claim 6, wherein the surface active agent is an alkali metal mono-n-propylbenzene sulphonate.

10. A method according to claim 6 wherein the surface active agent is an alkali metal diethylbenzene sulphonate.

11. A method according to claim 6, wherein the surface active agent is an alkali metal hexylbenzene sulphonate.

12. A method according to claim 5, wherein the surface active agent is a mixture of an alkali metal p-toluene sulphonate and an alkali metal mono-isopropylbenzene sulphonate and/or an alkali metal di-isopropylbenzene sulphonate; and/or an alkali metal tri-isopropylbenzene sulphonate; and/or an alkali metal n-butylbenzene sulphonate; and/or an alkali metal diethylbenzene sulphonate.

13. A method according to any one of the preceding claims wherein at least a part of the sand used in the composition of the mixture is constituted by regenerated sand, from which there has been eliminated at least a

BNSDOCID: <GB_____1361027A__I_>

part of the products which cover each grain of sand after the casting of the metal.

14. A method for producing foundry moulds and cores according to claim 1 substantially as hereinbefore described in any one of the accompanying examples.

MARKS & CLERK.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BNSDOCID: <GB_____1361027A__I_>

1361027 COMPLETE SPECIFICATION
9 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

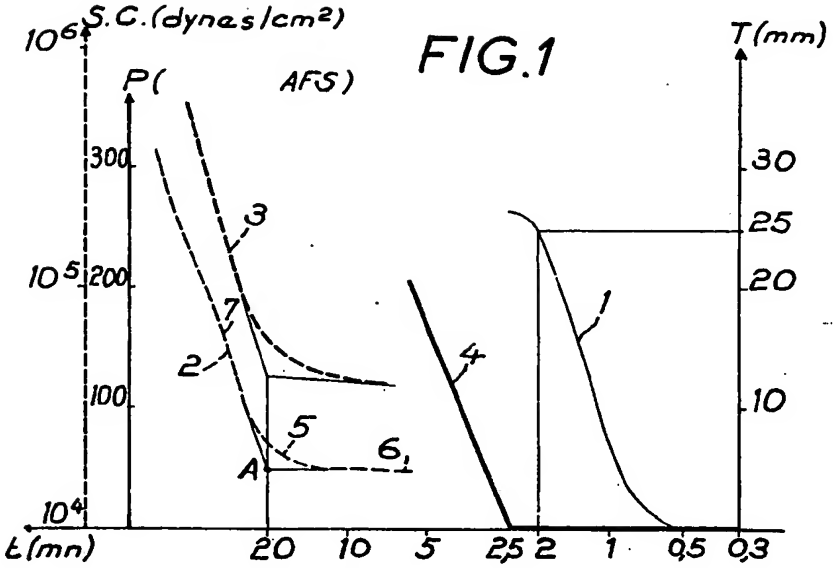


FIG.1

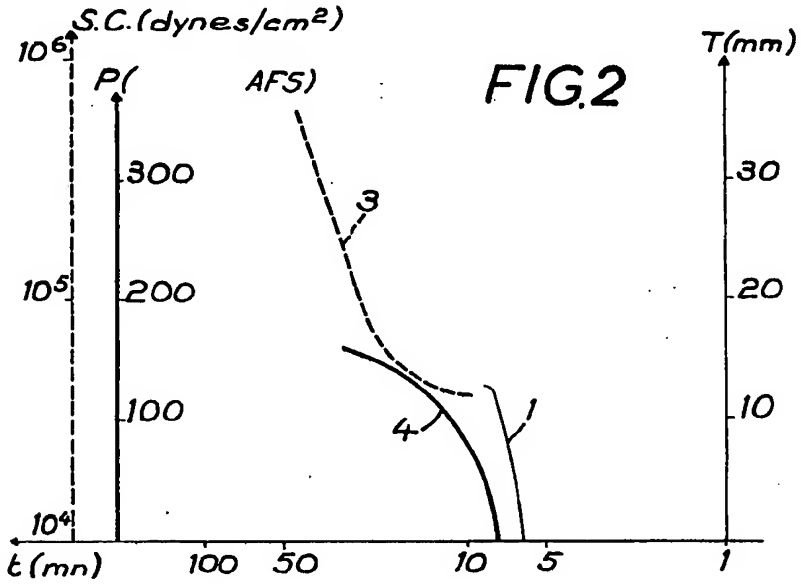


FIG.2

BNSDOCID: <GB_____1361027A__I_>

FIG.3

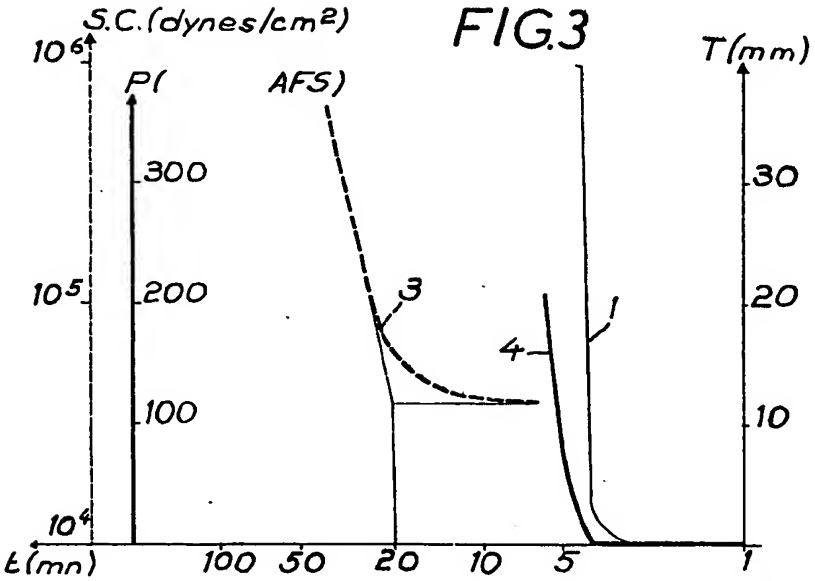
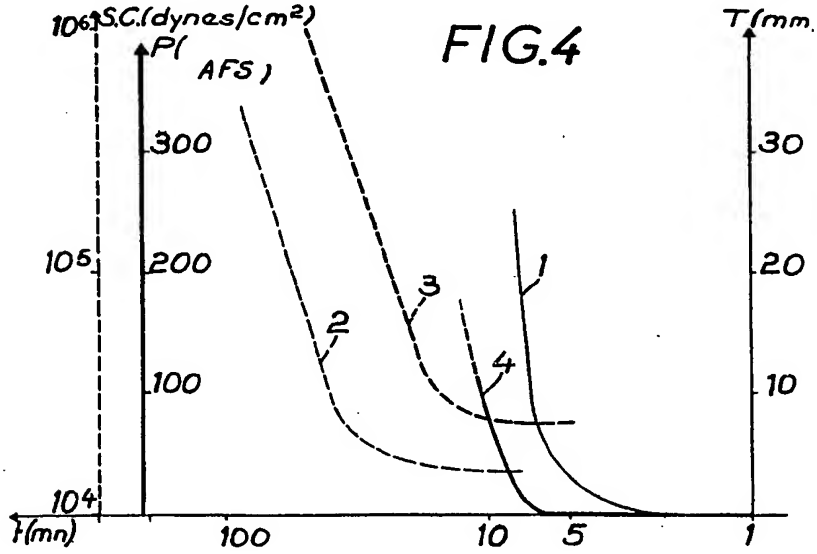


FIG.4



BNSDOCID: <GB_____1361027A__I_>

FIG.5

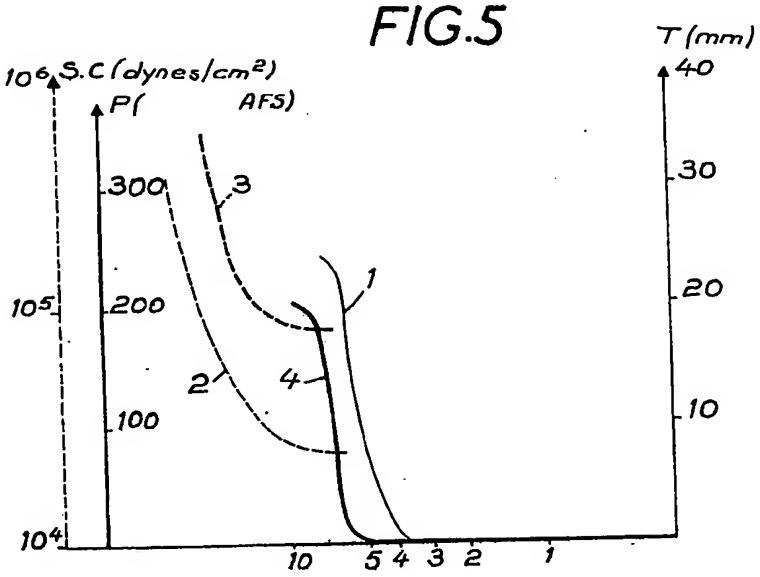
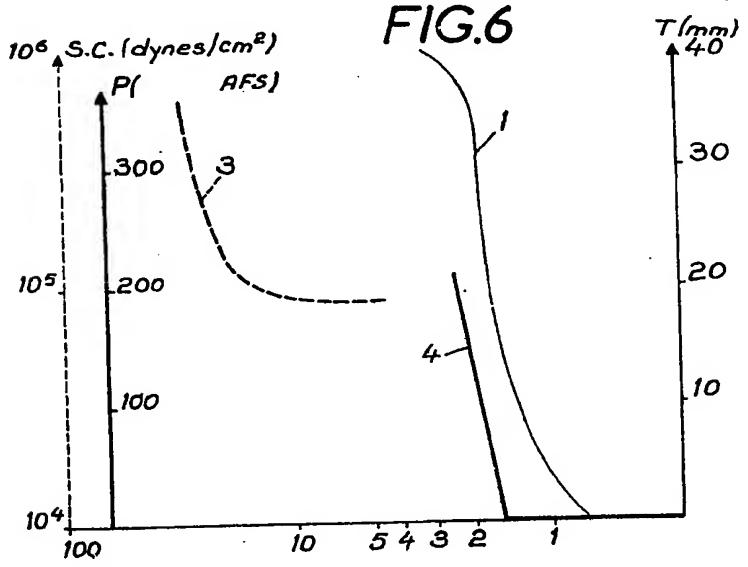


FIG.6



BNSDOCID: <GB_____1361027A__I_>

FIG.7

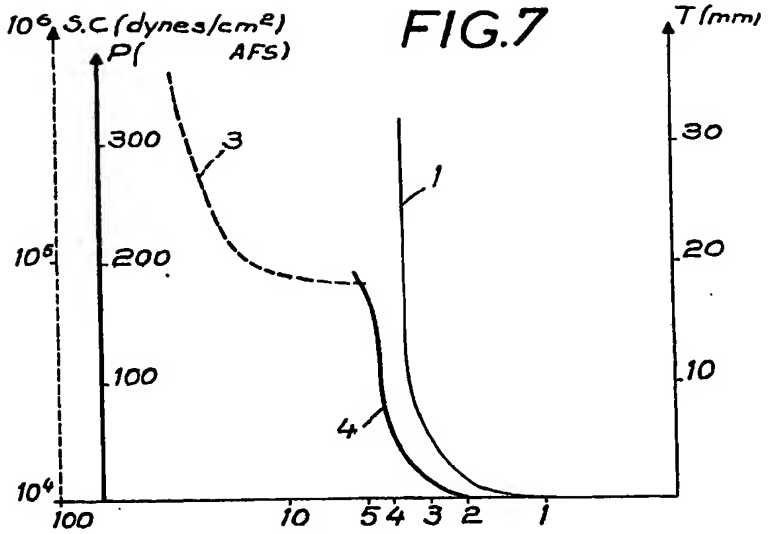
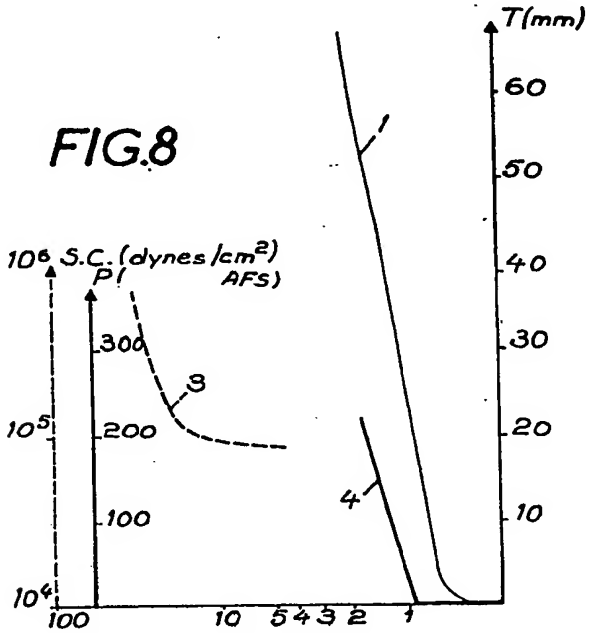


FIG.8



BNSDOCID: <GB_____1361027A__I_>

FIG.9

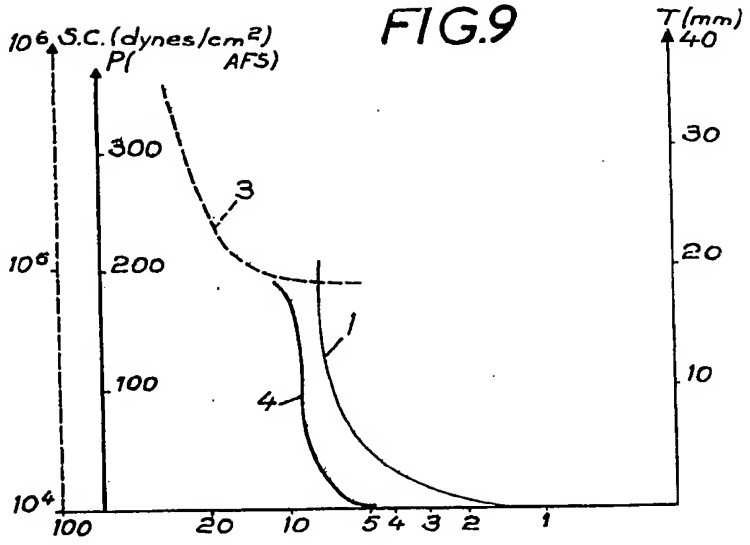
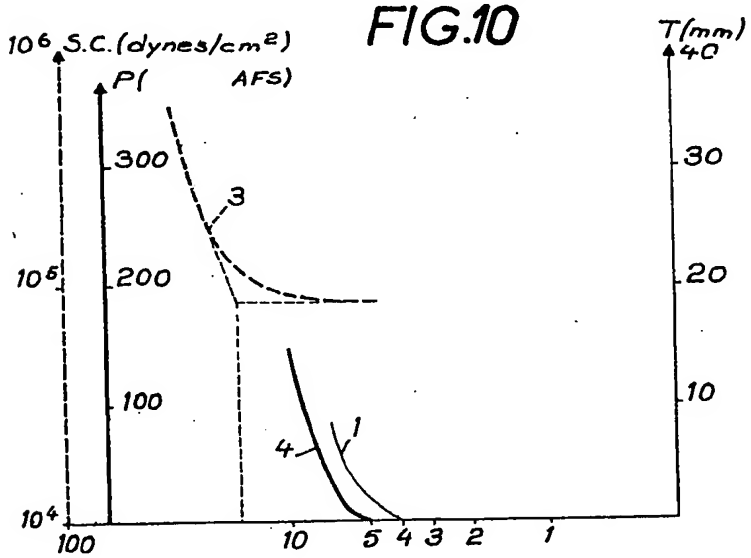


FIG.10



BNSDOCID: <GB_____1361027A__I_>

FIG.11

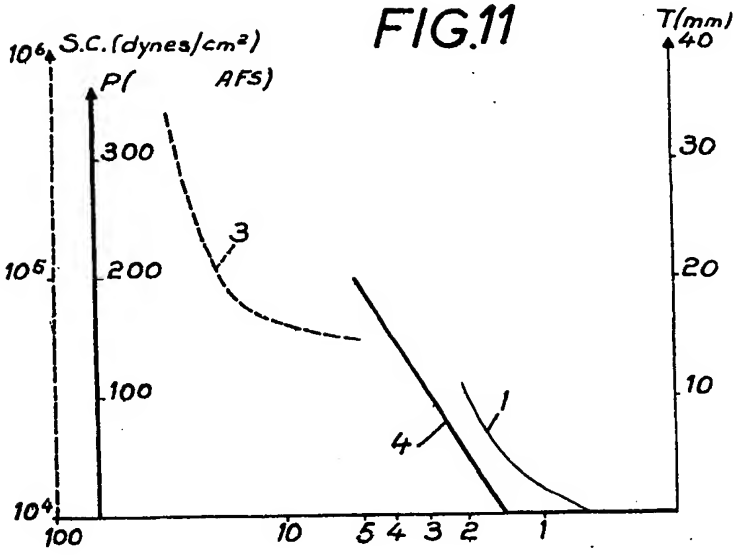
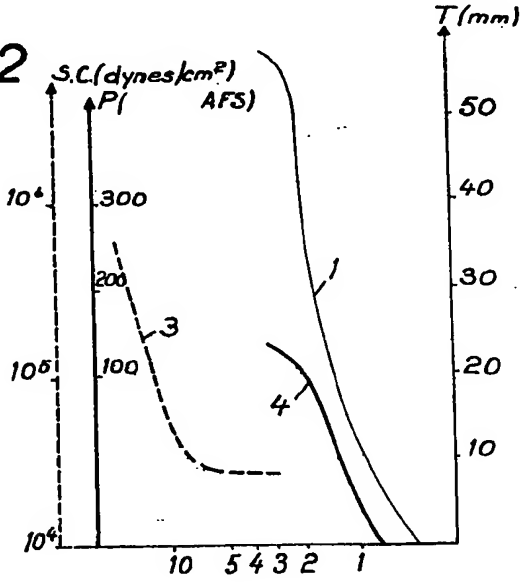


FIG.12



BNSDOCID: <GB_____1361027A__I_>

FIG.13

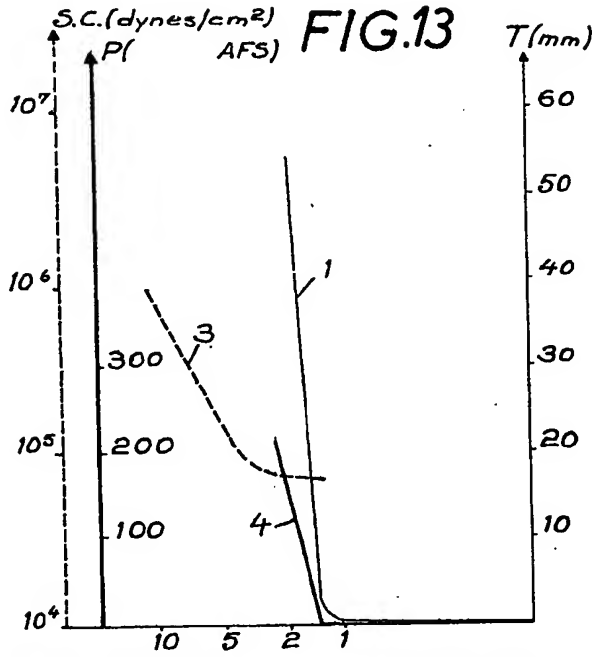
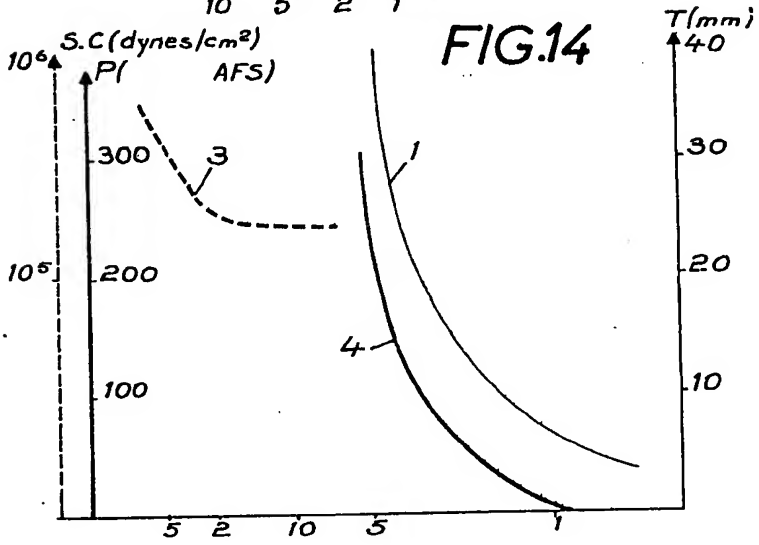
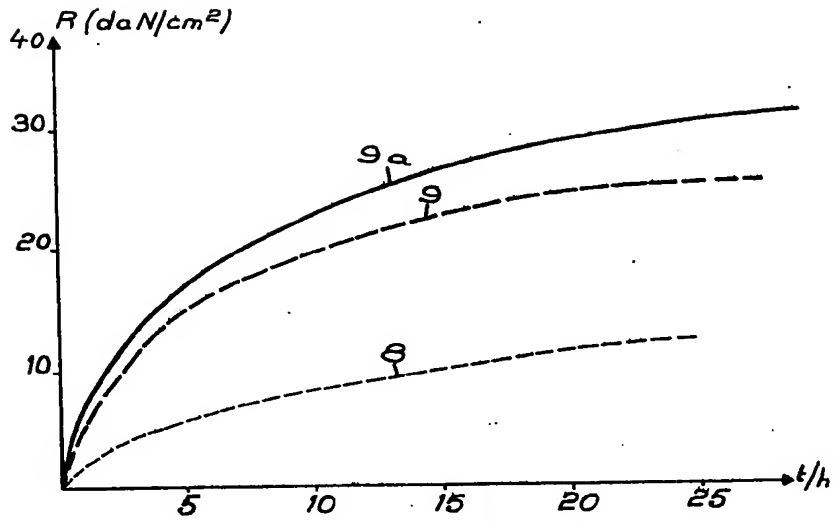


FIG.14



BNSDOCID: <GB_____1361027A__I_>

FIG.15



BNSDOCID: <GB_____1361027A__I_>

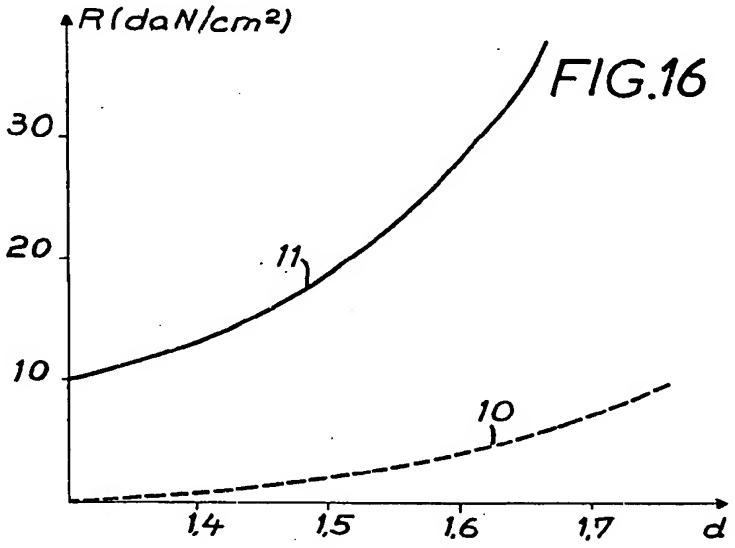


FIG.16

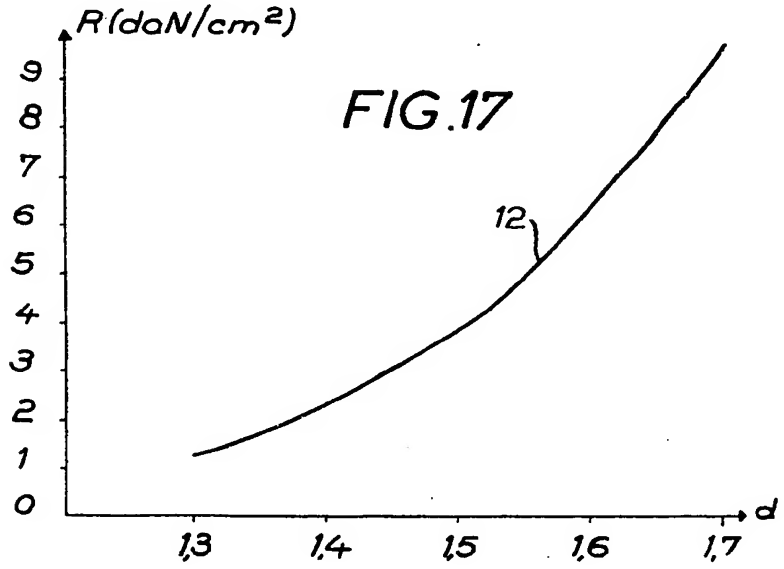


FIG.17

BNSDOCID: <GB_____1361027A__I_>